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(54) RESIN-ENCAPSULATED HIGH-BRIGHTNESS LIGHT EMITTING DIODE AND ITS MANUFACTURING METHOD

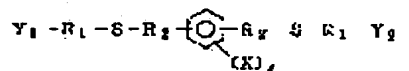
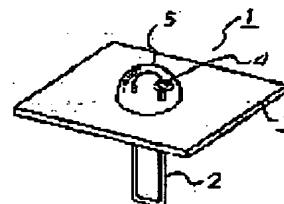
(57)Abstract:

PROBLEM TO BE SOLVED: To achieve high brightness and to improve heat resistance, moisture resistance, and durability by encapsulating a light emitting part with transparent resin with a high refraction made of polymer in at least one type of structure unit which is selected by a specific expression.

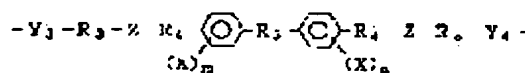
SOLUTION: Transparent resin 5 consists of resin having a refractive index of 1.55 or higher made of a polymer in at least one type of structure unit selected from expressions I and II.

In a light emitting diode 1, at least a light emitting part 4 is encapsulated with the transparent resin 5, where X represents a halogen atom excluding fluorine and I, m, and n are integers (0 or 1-4) in the expressions I and II.

Y1, Y2, Y3, and Y4 are connection groups and may be equal or different. Also, R1, R2, and R4 are alkylene and aralkylene groups which may contains O or S with 0 or 1-10 carbons. Z is either O or S and R3 is alkylene and aralkylene groups which may be container O or S with 1-10 carbons.



I



II

LEGAL STATUS

[Date of request for examination] 16.10.2001

[Date of sending the examiner's decision]

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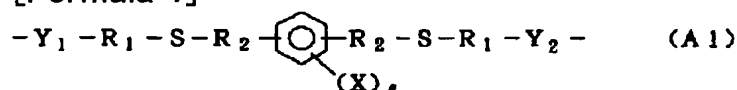
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 CLAIMS

[Claim(s)]

[Claim 1] Light emitting diode to which the closure of the light-emitting part was carried out for the refractive index which consists of a polymer of at least one sort of structural units chosen from the following general formula (A1) and a general formula (B1) at least with 1.55 or more transperence resin.

[Formula 1]

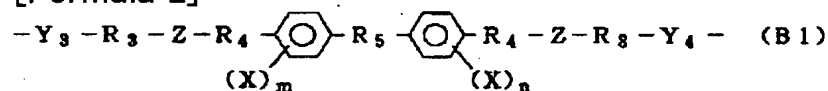


Xin [type: -- the halogen atom l:0 except a fluorine or the integer Y1 of 1-4, and

Y2 : By the joint radical, even if the same, you may differ.

R1, R2 : The alkylene group, aralkylene group which may contain O or S of 0 or carbon numbers 1-10.]

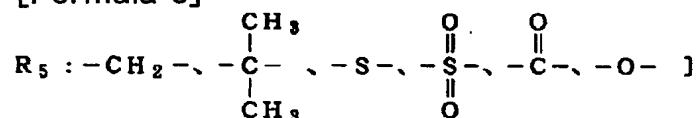
[Formula 2]



Xin [type: -- integer Z:0 of the halogen atom m except a fluorine, n:0, or 1-4 or SY3, and Y4 : By the joint radical, even if the same, you may differ.

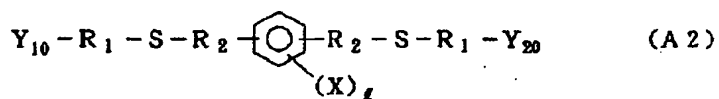
R3 : The alkylene group, aralkylene group R4 which may contain O or S of carbon numbers 1-10 : The alkylene group, aralkylene group which may contain O or S of 0 or carbon numbers 1-10.

[Formula 3]



[Claim 2] The manufacture approach of the light emitting diode characterized by a refractive index closing a light-emitting part at least by 1.55 or more transperence resin when a light energy line is irradiated and at least one sort of monomers chosen from the following general formula (A2) and a general formula (B-2) carry out polymerization hardening, where [of light emitting diode] a light-emitting part is immersed at least.

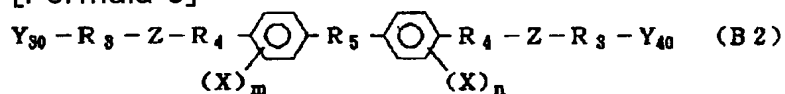
[Formula 4]



Xin [type: — by the halogen atom l:0 except a fluorine or the integer Y10 of 1-4, and the Y20: functional group, even if the same, you may differ.

R1 R2 : ARUKI which may contain O or S of 0 or carbon numbers 1-10 The Wren radical, aralkylene group.]

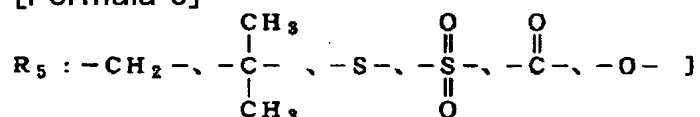
[Formula 5]



Xin [type: — by integer Z:0 of the halogen atom m except a fluorine, n:0, or 1-4 or SY30, and the Y40: functional group, even if the same, you may differ.

R3 : The alkylene group, aralkylene group R4 which may contain O or S of carbon numbers 1-10 : The alkylene group, aralkylene group which may contain O or S of 0 or carbon numbers 1-10.

[Formula 6]



[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to light emitting diodes used for an advertisement, lighting, a liquid crystal panel or optical communication, and an optical circuit, such as LED and LD (laser diode). By closing the semiconductor chip of a light emitting diode by specific resin, it is high brightness and these components that are excellent in heatproof and moisture-proof ** endurance are offered.

[0002]

[Description of the Prior Art] Many proposals which close light emitting diodes, such as LED and LD, with resin conventionally are made. The purpose divides roughly and is mentioned two. One is for preventing degradation by the factor from the external environment of a chip by the resin seal. LED and LD chip have the influence of generation of heat at the time of luminescence, and a front face has plentifully oxidation degradation and the case which reaction-deteriorates, carries out adhesion degradation or causes an open circuit according to ambient atmospheres, such as surrounding gas and moisture. These are prevented by the resin seal.

[0003] Other purposes are for gathering optical ejection effectiveness and attaining high brightness-ization. That is, refractive indexes are the light emitting diode semiconductor chip of 2-6, and that a refractive index eases the phenomenon in which a light reflex is performed in an interface with the air space of 1.0, and emission light from a chip cannot be taken out efficiently. In order to solve this problem, it is required for a refractive index to close a chip according to the transparence quality of the material which has the middle value of a chip and air. Although glass or resin is mentioned as the transparence quality of the material, in consideration of productivity, a resin seal is common and many closures especially by epoxy system thermosetting resin are proposed.

[0004] However, the periodic table which is represented by the GaAs system ingredient Much LED which begins the semi-conductor which consists of an III-V group, and is used industrially, and the refractive index of LD chip are the three to 5 neighborhoods, and 1.6-2.0, and the becoming high refractive-index resin are required of the refractive index of the optimal resin for reducing interface reflection with these chips and an air space. A refractive index is 1.4 to about 1.5,

and, as for existing closure resin, reduction of sufficient interface reflection, i.e., optical ejection, was not performed. In addition, a refractive index given in this invention is a value at the time of measuring at 25 degrees C using the D line (589nm) of Na.

[0005]

[Problem(s) to be Solved by the Invention] This invention is high brightness and it aims at offering the resin seal light emitting diode which is excellent in thermal resistance, moisture resistance, and endurance with sufficient productivity. In order to raise the brightness of light emitting diode, it is required to take out efficiently the light which emitted light in a front face. If this point is further stated to a detail, the refractive index and the optical fetch effectiveness of resin have the following relation.

[0006] namely, the refractive index n_0 of the semi-conductor whose optical ejection effectiveness is the ingredient of LED and LD, the refractive index n_1 of closure resin, and an external environment -- namely, -- usually -- refractive index n_2 of air from -- it can ask by calculating the reflection factor of the light in each interface, and optical ejection effectiveness becomes high, so that total of the reflection factor in each interface is small. When not carrying out a resin seal, it is this reflection factor R_0 . It is given by the degree type (1) in approximation.

[0007]

[Equation 1]

$$R_0 = \left(\frac{n_0 - n_2}{n_0 + n_2} \right)^2 \quad (1)$$

[0008] The total reflection factor R_1 at the time of carrying out a resin seal Since it is the sum of the reflection factor of a chip-resin interface and a resin-external world interface, it is given by the degree type (2) in approximation.

[0009]

[Equation 2]

$$R_1 = \left(\frac{n_0 - n_1}{n_0 + n_1} \right)^2 + \left(\frac{n_1 - n_2}{n_1 + n_2} \right)^2 \quad (2)$$

[0010] It is the refractive index n_0 of LED and LD chip here. It carries out and is the periodic table. Since the external environment of $n_0 = 3.66$ and a component is usually air when the GaAs system which consists of an III-V group is taken for an example, when $n_2 = 1.00$, it is the reflection R_0 when not carrying out a resin seal. It is set to $R_0 = 0.33$ from (1) type. That is, the light taken out effectively is LED and only 67% of the amount of luminescence of LD chip.

[0011] It is n_1 when it closes by high refractive-index resin on the other hand. When the time of being 1.70 is taken for an example, it is $R_1 = 0.23$ ($n_0 = 3.66$, $n_1 = 1.70$, $n_2 = 1.00$).

A next door and 77% of the amount of luminescence are taken out. Incidentally it is a reflection factor R_1 . It is [0012] from (2) types to become min.

[Equation 3]

$$n_1 = \sqrt{n_0} \cdot \sqrt{n_2} \quad (3)$$

[0013] It is at the ** time. That is, in the case of the above-mentioned example

($n_0 = 3.66$, $n_2 = 1.00$), at the time of $n_1 = 1.91$, a reflection factor serves as min and $R_1 = 0.20$ and 80% of the amount of luminescence of a chip are taken out of a system. Therefore, when using the semiconductor diode of a high refractive index, the resin of a high refractive index is needed.

[0014] Moreover, also in case LED and LD chip are closed in two steps using two resin with which refractive indexes differ, considering as a high refractive index is effective. That is, if the thing of a low refractive index is used as the 2nd step of closure resin which covers a it top, using high refractive-index resin as closure resin which touches a direct chip, the total reflection factor can be reduced further. For example, when the high refractive-index resin of refractive-index $n_1 = 1.70$ is used for the 1st step, the low refractive-index resin of refractive-index $n_1' = 1.40$ is used for the 2nd step and it closes, it is the total reflection factor R_2 . It is [0015] when the above-mentioned GaAs system is taken for an example.

[Equation 4]

$$R_2 = \left(\frac{n_0 - n_1}{n_0 + n_1} \right)^2 + \left(\frac{n_1 - n_1'}{n_1 + n_1'} \right)^2 + \left(\frac{n_1' - n_2}{n_1' + n_2} \right)^2 = 0.17$$

$$(n_0 = 3.66, n_1 = 1.70, n_1' = 1.40, n_2 = 1.00)$$

[0016] A next door and optical ejection effectiveness become 83%. Thus, even if it faces carrying out a resin seal in two or more steps, as for LED and the 1st step of resin which touches LD chip directly, it is desirable that it is a high refractive index. Although LED and the optical ejection effectiveness of LD chip have been guessed from the interface reflection factor above, high refractive-index-ization of closure resin enlarges, the include angle, i.e., the critical angle, of total reflection in a chip-resin interface, and contributes also to improvement in optical ejection effectiveness. The critical angle theta of total reflection [in / as shown in drawing 4 / the chip side D] (include angle which receives perpendicularly) is the refractive index n_0 of the semi-conductor layer A. Refractive index n_1 of closure resin It is given according to a degree type (4).

[0017]

[Equation 5]

$$\theta = \sin^{-1} \left(\frac{n_1}{n_0} \right) \quad (4)$$

[0018] That is, the refractive index of closure resin becomes large and it is n_1 . Refractive index n_0 of the semi-conductor layer A The range which the critical angle theta becomes large and carries out outgoing radiation to the resin layer C becomes large, so that it approaches. The critical angle theta becomes $\theta = 27.7$ degrees, when a GaAs system ($n_0 = 3.66$) is used as a semiconductor chip, and it closes by the resin of a refractive index 1.40 and closes by the resin of the $\theta = 22.5$ -degree refractive index 1.70 according to a formula (4). [0019] which can ask for the outgoing radiation area S on a chip side according to a degree type (5) from this include angle

[Equation 6] $S = \pi d \tan^2 \theta$ [0020] d is the thickness of the semi-conductor layer A here. Outgoing radiation area S2 at the time of closing by the outgoing

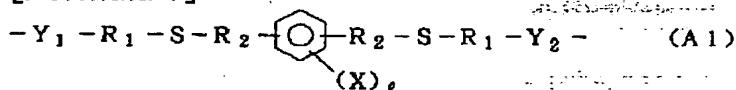
radiation area S1 at the time of closing by the resin of the above-mentioned refractive index 1.40, and the resin of a refractive index 1.70 It turns out that it is set to $S1 = 0.171$ and $S2 = 0.275$, respectively, and outgoing radiation area becomes large about 1.6 times by high refractive-index-ization of resin. That is, the light which carried out outgoing radiation from the PN-junction side of a semiconductor chip can be taken out efficiently.

[0021]

[Means for Solving the Problem] this invention persons found out that optical ejection effectiveness improved and light emitting diodes, such as LED of high brightness and LD component, were obtained with sufficient productivity by closing light emitting diode with the specific transparence resin of high refraction, as a result of inquiring wholeheartedly, in order to solve the above-mentioned technical problem. Moreover, by using for intramolecular the polyfunctional light and/or thermosetting resin which have two or more polymerization nature functional groups, the component which is excellent in thermal resistance, moisture resistance, and endurance can be manufactured. This invention is in the light emitting diode to which the closure of the light-emitting part was carried out at least with the with a refractive indexes of 1.55 or more which consist of a polymer of the structural unit more than a kind at least transparence resin chosen from the following general formula (A1) and a general formula (B1).

[0022]

[Formula 7]

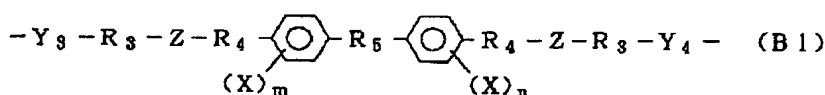


[0023] Xin [type: -- the halogen atom:0 except a fluorine or the integer Y1 of 1-4, and Y2 : By the joint radical, even if the same, you may differ.

R1, R2 : The alkylene group, aralkylene group which may contain O or S of 0 or carbon numbers 1-10.]

[0024]

[Formula 8]

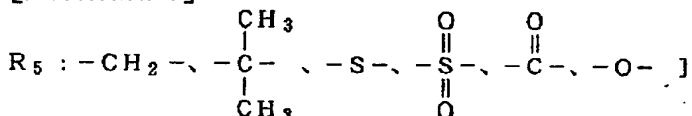


[0025] Xin [type: -- integer Z:0 of the halogen atom m except a fluorine, n:0, or 1-4 or SY3, and Y4 : By the joint radical, even if the same, you may differ.

R3 : The alkylene group, aralkylene group R4 which may contain O or S of carbon numbers 1-10 : The alkylene group, aralkylene group which may contain O or S of 0 or carbon numbers 1-10.

[0026]

[Formula 9]



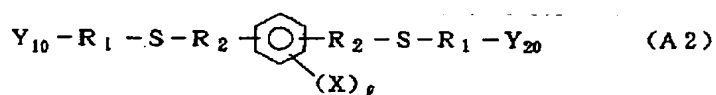
[0027] In order to attain high refractive-index-ization of resin generally, it is effective if ** ring, ** sulfur atom, and the halogen atom except ** fluorine are introduced into a molecule frame or a chain. this invention persons checked that it could be used as a monomer (A2) effective in this invention, and (B-2) by making each one or more ends combine with the both-ends section of these structural units light and/or the functional group which carries out thermal polymerization by the above-mentioned formula (A1) and (B1) paying attention to the resin which has the structural unit by which a formula is carried out serving as a high refractive index.

[0028]

[Embodiment of the Invention] With a refractive indexes of 1.55 or more transparence resin usable as closure resin of this invention is obtained light and/or by carrying out heat curing in the transparency liquid monomer of the following general formula (A2) and a general formula (B-2).

[0029]

[Formula 10]

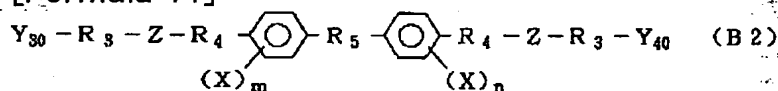


[0030] Xin [type: -- by the halogen atom l:0 except a fluorine or the integer Y10 of 1-4, and the Y20: functional group, even if the same, you may differ.

R1, R2 : The alkylene group, aralkylene group which may contain O or S of 0 or carbon numbers 1-10.]

[0031]

[Formula 11]

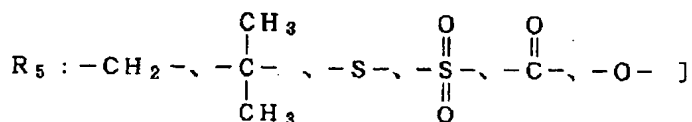


[0032] Xin [type: -- by integer Z:0 of the halogen atom m except a fluorine, n:0, or 1-4 or SY30, and the Y40: functional group, even if the same, you may differ.

R3 : The alkylene group, aralkylene group R4 which may contain O or S of carbon numbers 1-10 : The alkylene group, aralkylene group which may contain O or S of 0 or carbon numbers 1-10.

[0033]

[Formula 12]

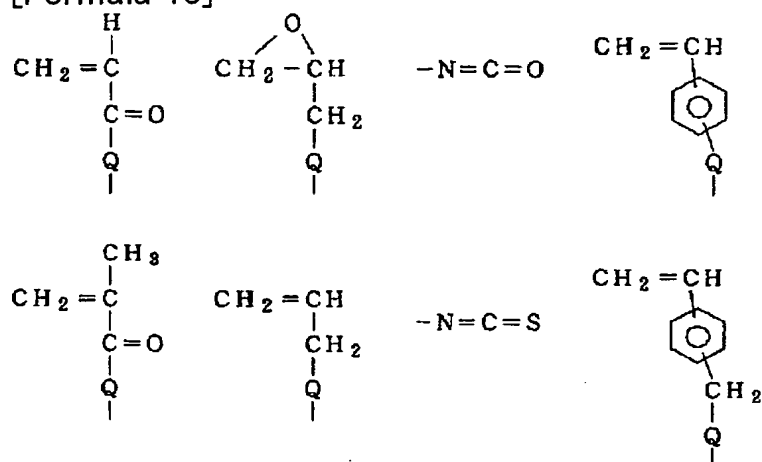


[0034] As polymerization nature functional groups Y10, Y20, Y30, and Y40, an acryloyl radical as (meta) shown by the degree type, a glycidyl group, an aryl group, an isocyanate radical, an isothiocyanate radical, a vinyl phenyl group, a vinylbenzyl radical, etc. are mentioned. These monomers are polyfunctional monomers which have two or more polymerization nature functional groups in intramolecular, and the polymer is excellent in thermal resistance and moisture resistance as a photo-

setting resin or thermosetting resin.

[0035]

[Formula 13]

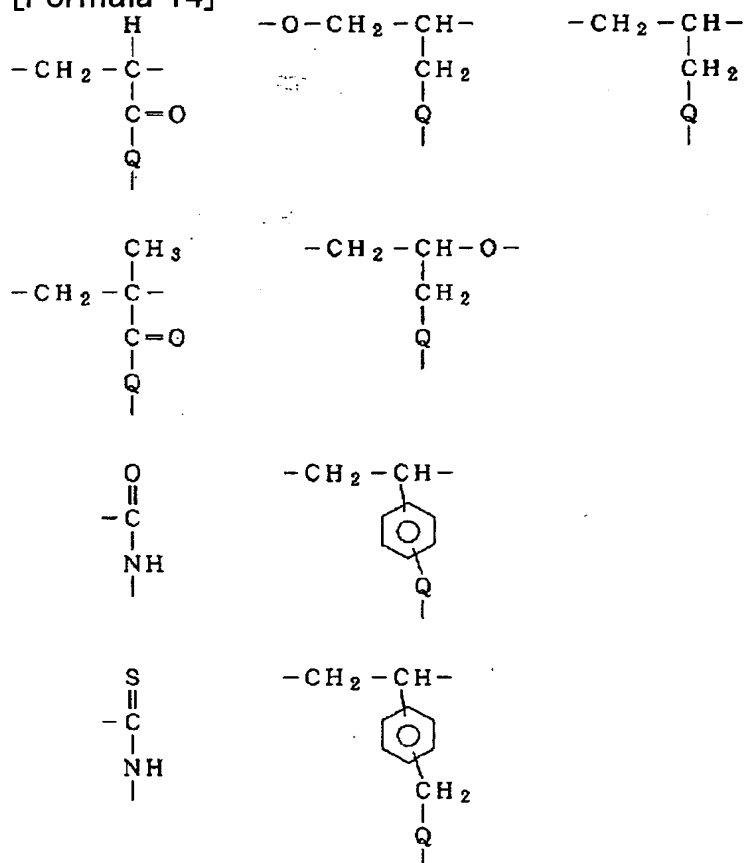


QはS又はO

[0036] Therefore, the joint radicals Y1, Y2, Y3, and Y4 serve as the following structure.

[0037]

[Formula 14]



QはS又はO

As a monomer which has the structural unit of a general formula (A2) For example,

p-screw (beta-(meta) acryloyloxyethyl thio) xylylene, m-screw (beta-(meta) acryloyloxyethyl thio) xylylene, p-screw (beta-(meta) acryloyloxyethyl thio ethyl thio) xylylene, m-screw (beta-(meta) acryloyloxyethyl thio ethyl thio) xylylene, p-screw (beta-(meta) acryloyloxyethyl oxy-ethyl thio) xylylene, m-screw (beta-(meta) acryloyloxyethyl oxy-ethyl thio) xylylene, alpha and alpha'-screw (beta-(meta) acryloyloxyethyl thio) - 2, 3, 5, 6-tetra-chloro-p-xylylene, alpha and alpha'-screw (beta-(meta) acryloyloxyethyl thio) - 2, 3, 5, 6-tetra-chloro-m-xylylene, alpha and alpha'-screw (beta-(meta) acryloyloxyethyl thio) - 2, 3, 5, 6-tetrabromo-p-xylylene, alpha and alpha'-screw (beta-(meta) acryloyloxyethyl thio) - 2, 3, 5, 6-tetrabromo-m-xylylene, p-screw (beta-(meta) acryloyl thio ethyl thio) xylylene, m-screw (beta-(meta) acryloyl thio ethyl thio) xylylene, p-screw (beta-(meta) acryloyl thio ethyl CHIOECHIRUCHIO) xylylene, m-screw (beta-(meta) acryloyl thio ethyl CHIOECHIRUCHIO) xylylene, p-screw (beta-(meta) acryloyl thio ethyloxy ECHIRUCHIO) xylylene, m-screw (beta-(meta) acryloyl thio ethyloxy ECHIRUCHIO) xylylene, alpha and alpha'-screw (beta-(meta) acryloyl thio ethyl thio) - 2, 3, 5, 6-tetra-chloro-p-xylylene, alpha and alpha'-screw (beta-(meta) acryloyl thio ethyl thio) - 2, 3, 5, 6-tetra-chloro-m-xylylene, alpha and alpha'-screw (beta-(meta) acryloyl thio ethyl thio) - 2, 3, 5, 6-tetrabromo-p-xylylene, alpha and alpha'-screw (beta-(meta) acryloyl thio ethyl thio) - 2, 3, 5, a di(meth) acrylate compound like the 6-tetrabromo-m-xylylene, [0038] p-screw (beta-glycidyloxy ethyl thio) xylylene, m-screw (beta-glycidyloxy ethyl thio) xylylene, The epoxy compound of p-screw (beta-glycidyl thio ethyl thio) xylylene and m-screw (beta-glycidyl thio ethyl thio) xylylene, The diaryl compound of p-screw (beta-allyloxy ethyl thio) xylylene, m-screw (beta-allyloxy ethyl thio) xylylene, p-screw (beta-arylthio ethyl thio) xylylene, and m-screw (beta-arylthio ethyl thio) xylylene, [0039] The diisocyanate compound of p-screw (beta-isocyanato ethyl thio) xylylene and m-screw (beta-isocyanato ethyl thio) xylylene, The JIISO thiocyanate compound of p-screw (beta-iso CHIOSHIANATO ethyl thio) xylylene and m-screw (beta-iso CHIOSHIANATO ethyl thio) xylylene, p-screw [2-(4-vinyl phenyloxy) ethyl thio] xylylene, m-screw [2-(4-vinyl phenyloxy) ethyl thio] xylylene, p-screw [2-(4-vinyl phenylthio) ethyl thio] xylylene, m-screw [2-(4-vinyl phenylthio) ethyl thio] xylylene, p-screw [2-(4-vinylbenzyl oxy-) ethyl thio] xylylene, A styrene system compound like m-screw [2-(4-vinylbenzyl oxy-) ethyl thio] xylylene, p-screw [2-(4-vinylbenzyl thio) ethyl thio] xylylene, and m-screw [2-(4-vinylbenzyl thio) ethyl thio] xylylene is mentioned.

[0040] As a monomer which has the structural unit of a general formula (B-2) For example, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio) diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyl thio) diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyl thio) diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio) -3, 3', 5, and 5'-tetrabromo diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyl thio) -3, 3', 5, and 5'-tetrabromo diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyl thio) -3, 3', 5, and 5'-tetrabromo diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyloxy) diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyloxy) diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-) -3, 3', 5, and 5'-

tetrabromo diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyloxy) -3, 3', 5, and 5'-tetrabromo diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyloxy) -3, 3', 5, and 5'-tetrabromo diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyl thio ethyl thio) diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyl thio ethyl CHIOECHIRUCHIO) diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy ECHIRUCHIO) diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyl thio ethyl thio) -3, 3', 5, and 5'-tetrabromo diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyl thio ethyl CHIOECHIRUCHIO) -3, 3', 5, and 5'-tetrabromo diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy ECHIRUCHIO) -3, 3', 5, and 5'-tetrabromo diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy) diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyl thio ECHIRUCHIO ethyloxy) diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy ethyloxy) diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy) -3, 3', 5, and 5'-tetrabromo diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyl thio ECHIRUCHIO ethyloxy) -3, 3', 5, and 5'-tetrabromo diphenylsulfone, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy ethyloxy) -3, 3', 5, and 5'-tetrabromo diphenylsulfone, A 4 and 4'-screw (2-(meta) acryloyloxyethyl thio) diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyl thio) diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyl thio) diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyloxyethyl thio) -3, 3', 5, and 5'-tetrabromo diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyl thio) -3, 3', 5, and 5'-tetrabromo diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyl thio) -3, 3', 5, and 5'-tetrabromo diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-) diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyloxy) diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyloxy) diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-) -3, 3', 5, and 5'-tetrabromo diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyloxy) -3, 3', 5, and 5'-tetrabromo diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyloxy) -3, 3', 5, and 5'-tetrabromo diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyl thio ethyl thio) diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyl thio ethyl CHIOECHIRUCHIO) diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy ECHIRUCHIO) diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyl thio ethyl thio) -3, 3', 5, and 5'-tetrabromo diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyl thio ethyl CHIOECHIRUCHIO) -3, 3', 5, and 5'-tetrabromo diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy ECHIRUCHIO) -3, 3', 5, and 5'-tetrabromo diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy) diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyl thio ECHIRUCHIO ethyloxy) diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy ethyloxy) diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy) -3, 3', 5, and 5'-tetrabromo diphenyl sulfide, A 4 and 4'-screw (2-(meta) acryloyl thio ECHIRUCHIO ethyloxy) -3, 3', 5, and 5'-tetrabromo diphenyl sulfide, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio) JIFENIRUKE Ton, 4, and 4'-screw (2-(meta) acryloyloxyethyl thio ethyl thio) diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyl thio) diphenyl ketone, 4 and 4'-

screw (2-(meta) acryloyloxyethyl thio) -3, 3', 5, and 5'-tetrabromo diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyl thio) -3, 3', 5, and 5'-tetrabromo diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyl thio) 3, 3', 5, and 5'-tetrabromo diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-) diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyloxy) diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyloxy) diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-) -3, 3', 5, and 5'-tetrabromo diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyl thio oxy-) -3, 3', 5, and 5'-tetrabromo diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyloxy) 3, 3', 5, and 5'-tetrabromo diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyl thio ethyl thio) diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyl thio ethyl CHIOECHIRUCHIO) diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy ECHIRUCHIO) diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyl thio ethyl thio) -3, 3', 5, and 5'-tetrabromo diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyl thio ethyl CHIOECHIRUCHIO) -3, 3', 5, and 5'-tetrabromo diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy ECHIRUCHIO) -3, 3', 5, and 5'-tetrabromo diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy) diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyl thio ECHIRUCHIO ethyloxy) diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy ethyloxy) diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy) -3, 3', 5, and 5'-tetrabromo diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyl thio ethyl CHIOECHIRUCHIOOKISHI) -3, 3', 5, and 5'-tetrabromo diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy ethyloxy) 3, 3', 5, and 5'-tetrabromo diphenyl ketone, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio) diphenylmethane, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyl thio) diphenylmethane, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyl thio) diphenylmethane, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio) -3, 3', 5, and 5'-tetrabromo diphenylmethane, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyl thio) -3, 3', 5, and 5'-tetrabromo diphenylmethane, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyl thio) -3, 3', 5, and 5'-tetrabromo diphenylmethane, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-) diphenylmethane, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyloxy) diphenylmethane, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyloxy) diphenylmethane, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-) -3, 3', 5, and 5'-tetrabromo diphenylmethane, 4 and 4'-screw (2-(meta) acryloyloxyethyl thio ethyloxy) -3, 3', 5, and 5'-tetrabromo diphenylmethane, 4 and 4'-screw (2-(meta) acryloyloxyethyl oxy-ethyloxy) -3, 3', 5, and 5'-tetrabromo diphenylmethane, 4 and 4'-screw (2-(meta) acryloyl thio ethyl thio) diphenylmethane, 4 and 4'-screw (2-(meta) acryloyl thio ethyl CHIOECHIRUCHIO) diphenylmethane, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy ECHIRUCHIO) diphenylmethane, 4 and 4'-screw (2-(meta) acryloyl thio ethyl thio) -3, 3', 5, and 5'-tetrabromo diphenylmethane, 4 and 4'-screw (2-(meta) acryloyl thio ethyl CHIOECHIRUCHIO) -3, 3', 5, and 5'-tetrabromo diphenylmethane, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy ECHIRUCHIO) -3, 3', 5, and 5'-tetrabromo diphenylmethane, 4 and 4'-screw (2-(meta) acryloyl thio ECHIRUCHIO ethyloxy) diphenylmethane, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy) diphenylmethane, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy)

ethyloxy) diphenylmethane, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy) -3, 3', 5, and 5'-tetrabromo diphenylmethane, 4 and 4'-screw (2-(meta) acryloyl thio ECHIRUCHIO ethyloxy) -3, 3', 5, and 5'-tetrabromo diphenylmethane, 4 and 4'-screw (2-(meta) acryloyl thio ethyloxy ethyloxy) 3, 3', 5, and 5'-tetrabromo diphenylmethane, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl thio) phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl thio ethyl thio) phenyl] propane, 2, 2-screw [4 - (beta-(meta) acryloyloxyethyl oxy-ethyl) Thio phenyl] propane, 2, and 2-screw [4-(beta-(meta) acryloyloxyethyl thio)-3, 3', 5, and 5'-tetrabromo phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl thio ethyl thio)-3, 3', 5, and 5'-tetrabromo phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl oxy-ethyl thio)-3, 3', 5, and 5'-tetrabromo phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl oxy-) phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl thio ethyloxy) phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl oxy-ethyloxy) phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl oxy-)-3, 3', 5, and 5'-tetrabromo diphenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl thio ethyloxy)-3, 3', 5, and 5'-tetrabromo phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl oxy-ethyloxy)-3, 3', 5, and 5'-tetrabromo diphenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyl thio) phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyl CHIOECHIRUCHIO) phenyl] propane, 2 and 2-screw [4- (a beta-(meta) acryloyl CHIOECHIRUOKISHI ethyl thiophenyl] propane - -) 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyl thio)-3, 3', 5, and 5'-tetrabromo phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyl CHIOECHIRUCHIO)-3, 3', 5, and 5'-tetrabromo phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyloxy ECHIRUCHIO)-3, 3', 5, and 5'-tetrabromo phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyloxy) phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyl thio ECHIRUCHIO ethyloxy) phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyloxy ethyloxy) phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyloxy)-3, 3', 5, and 5'-tetrabromo phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyl thio ECHIRUCHIO ethyloxy)-3, 3', 5, and 5'-tetrabromo phenyl] propane, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl thio ethyl thio) phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl oxy-ethyl thio) phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl thio)-3, 3', 5, and 5'-tetrabromo phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl thio ethyl thio)-3, 3', 5, and 5'-tetrabromo phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl oxy-ethyl thio)-3, 3', 5, and 5'-tetrabromo phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl thio ethyloxy) phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl oxy-ethyloxy) phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl oxy-)-3, 3', 5, and 5'-tetrabromo diphenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl thio ethyloxy)-3, 3', 5, and 5'-tetrabromo phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyloxyethyl oxy-ethyloxy)-3, 3', 5, and 5'-tetra-BUROJI phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyl thio) phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyl CHIOECHIRUCHIO) phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyl thio

ethyloxy ECHIRUCHIO) phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyl thio)-3, 3', 5, and 5'-tetrabromo phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyl CHIOECHIRUCHIO)-3, 3', 5, and 5'-tetrabromo phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyloxy ECHIRUCHIO)-3, 3', 5, and 5'-tetrabromo phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyloxy) phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyl thio ECHIRUCHIO ethyloxy) phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyloxy ethyloxy) phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyloxy)-3, 3', 5, and 5'-tetrabromo phenyl] ether, 2 and 2-screw [4-(beta-(meta) acryloyl thio ECHIRUCHIO ethyloxy)-3, 3', 5, and 5'-tetrabromo phenyl] ether, An acrylate compound like 2 and 2-screw [4-(beta-(meta) acryloyl thio ethyloxy ethyloxy)-3, 3', 5, and 5'-tetrabromo phenyl] ether (meta), [0041] 4 and 4'-screw (2-glycidyloxy ethyl thio) diphenylsulfone, 4, and 4'-screw (2-glycidyloxy ethyloxy) diphenylsulfone, 2, and 2-screw [4-(beta-glycidyloxy ethyl thio) phenyl] propane, 2, 2-screw [4 - (beta-GU) The epoxy compound of RISHIJIRU oxy-ethyl OKISHIO phenyl] propane, 4, and 4'-screw (2-glycidyl thio ethyl thio) diphenylsulfone, 4, and 4'-screw (2-glycidyl thio ethyloxy) diphenylsulfone, 2, and 2-screw [4-(beta-glycidyl thio ethyl thio) phenyl] propane, 2, and 2-screw [4-(beta-glycidyl thio ethyloxy) phenyl] propane, [0042] 4 and 4'-screw (2-allyloxy ethyl thio) diphenylsulfone, 4 and 4'-screw (2-allyloxy ethyloxy) diphenylsulfone, 2 and 2-screw [4-(beta-allyloxy ethyl thio) phenyl] propane, 2 and 2-screw [4-(beta-allyloxy ethyloxy) phenyl] propane, 4 and 4'-screw (2-arylthio ethyl thio) diphenylsulfone, The diaryl compound of 4 and 4'-screw (2-arylthio ethyloxy) diphenylsulfone, 2, and 2-screw [4-(beta-arylthio ethyl thio) phenyl] propane, 2, and 2-screw [4-(beta-arylthio ethyloxy) phenyl] propane, [0043] The diisocyanate compound of 4 and 4'-screw (2-isocyanato ethyl thio) diphenylsulfone, 4, and 4'-screw (2-isocyanato ethyloxy) diphenylsulfone, 2, and 2-screw [4-beta-isocyanato ethyl thio phenyl] propane, 2, and 2-screw [4-beta-isocyanato ethyloxy phenyl] propane, [0044] The JIISO thiocyanate compound of 4 and 4'-screw (2-iso CHIOSHIANATO ethyl thio) diphenylsulfone, 4, and 4'-screw (2-iso thio SHIANATO ethyloxy) diphenylsulfone, 2, and 2-screw [4-beta-iso CHIOSHIANATO ethyl thio phenyl] propane, 2, and 2-screw [4-beta-iso thio SHIANATO ethyloxy phenyl] propane, [0045] 4 and 4'-screw [2-(4-vinyl phenyloxy) ethyl thio] diphenylsulfone, 4 and 4'-screw [2-(4-vinyl phenyloxy) ethyloxy] diphenylsulfone, 2 and 2-screw [4-[2-(4-vinyl phenyloxy) ethyl thio] phenyl] propane, 2 and 2-screw [4-[2-(4-vinyl phenyloxy) ethyloxy] phenyl] propane, 4 and 4'-screw [2-(4-vinyl phenylthio) ethyl thio] diphenylsulfone, 4 and 4'-screw [2-(4-vinyl phenylthio) ethyloxy] diphenylsulfone, 2 and 2-screw [4-[2-(4-vinyl phenylthio) ethyl thio] phenyl] propane, 2 and 2-screw [4-[2-(4-vinyl phenylthio) ethyloxy] phenyl] propane, 4 and 4'-screw [2-(4-vinylbenzyl oxy-) ethyl thio] diphenylsulfone, 4 and 4'-screw [2-(4-vinylbenzyl oxy-) ethyloxy] diphenylsulfone, 2 and 2-screw [4-[2-(4-vinylbenzyl oxy-) ethyl thio] phenyl] propane, 2 and 2-screw [4-[2-(4-vinylbenzyl oxy-) ethyloxy] phenyl] propane, 4 and 4'-screw [2-(4-vinylbenzyl thio) ethyl thio] diphenylsulfone, 4 and 4'-screw [2-(4-vinylbenzyl thio) ethyloxy] diphenylsulfone, A styrene system compound like 2 and 2-screw [4-[2-(4-vinylbenzyl thio) ethyl thio] phenyl] propane, 2, and 2-screw [4-[2-(4-vinylbenzyl thio) ethyloxy] phenyl]

propane is mentioned.

[0046] These desirable are di(meth)acrylate compounds and especially a desirable thing is p-screw (beta-methacryloyloxy-ethyl thio) xylylene and p-screw (it is the constituent of beta-methacryloyl thio ECHIRUCHIONO xylylene, 4, and 4'-screw (2-methacryloyloxy-ethyl thio) diphenylsulfone, 4, and 4'-screw (2-methacryloyl thio ethyl thio) diphenylsulfone, and a these monomers and the monomer which can be copolymerized.).

[0047] As the monomer and the monomer which can be copolymerized which has the structural unit of a general formula (A2) and/or a general formula (B-2) For example, methyl (meta) acrylate, phenyl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, a methacryloyloxy methyl tetracyclo decane, Methacryloyl oxymethyl tetracyclo dodecen, ethylene GURIKORUJI (meta) acrylate, A 1, 6-hexane JIORUJI (meta) acrylate, 2, and 2'-screw [4-(beta-methacryloyloxy ethoxy) cyclohexyl] propane, 1, 4-screw (methacryloyloxy methyl) cyclohexane, TORIMECHI roll pro pantry (meta) acrylate, Styrene, KURORU styrene, alpha methyl styrene, the acrylate compound and styrene system compound like a divinylbenzene, Pentaerythritol tetrakis (beta-thiopropionate), pentaerythritol tetrakis (beta-thioglycolate), Trimethylol propane tris (beta-thiopropionate), trimethylol propane tris (beta-thioglycolate), A diethylene-glycol screw (beta-thiopropionate), a diethylene-glycol screw (beta-thioglycolate), A triethylene glycol screw (beta-thiopropionate), a triethylene glycol screw (beta-thioglycolate), Dipentaerythritol hexa kiss (beta-thiopropionate), dipentaerythritol hexa.kiss (beta-thioglycolate), Tris [2-(beta-thio propionyloxy) ethyl] TORIISOSHIA nurate, Tris [2-(beta-thio propionyloxy ethoxy) ethyl] TORIISOSHIA nurate, Tris [3-(beta-thio propionyloxy) propyl] TORIISOSHIA nurate, Tris (2-thio GURIKONIRU oxy-ethyl) TORIISOSHIA nurate, Tris (2-thio GURIKONIRU oxyethoxy ethyl) TORIISOSHIA nurate, The poly thiol of a tris (3-thio GURIKONIRU oxy-propyl) TORIISOSHIA nurate, BENZENJI mercaptan, xylylene JIMERU captan, 4, and 4'-dimercapto diphenyl sulfide, well-known polyol, etc. are mentioned. When a diisocyanate compound and a JIISO thiocyanate compound are used as a monomer which has the structural unit of a general formula (A2) and/or (B-2), the poly thiol or polyol compound which carries out addition polymerization to these compounds is desirable. The amount of the poly thiol to be used or polyol is set up so that the total number of functional groups may become almost the same as the total number of functional groups of isocyanate or isothiocyanate.

[0048] The amount of the monomer and the monomer which can be copolymerized used which has the structural unit of these general formulas (A2) and/or a general formula (B-2) is set up so that the refractive index of the resin with which a weight ratio is 80% or less of a total presentation, and hardened the constituent may become 1.55 or more. As an initiator used light and/or in case heat curing is carried out, although a radical polymerization initiator well-known as a photopolymerization agent and a cationic initiator are used, for example, these constituents 2, 6-dimethylbenzoyl diphenyl phosphine oxide, 2 and 4, 6-trimethyl benzoyl diphenyl phosphine oxide, 2, 4, 6-trimethyl benzoyl phenyl phosphinic acid methyl ester, Acyl phosphine oxide and acyl phosphinate, such as 2, 6-dichloro benzoyl phenyl phosphine oxide, 2, and 6-JIMECHITOKISHI benzoyl diphenyl

phosphine oxide, 1-phenyl-2-hydroxy-isobutane-1-ON, 1-hydroxy cyclohexyl phenyl ketone, 4-JIFENOKISHI dichloro acetophenone, a diethoxy acetophenone, Acetophenone system compounds, such as 1-(4-isopropyl phenyl)-2-hydroxy-isobutane-1-ON, And a benzophenone, 4-phenylbenzo phenon, benzoylbenzoic acid MECHIRUCHI, 4-phenylbenzo phenon, hydroxy benzophenone, 3, and 3'-dimethyl-4-methoxybenzophenone, There are benzophenone system compounds, such as a JIFENOKISHI benzophenone, aromatic series diazonium salt, aromatic series sulfonium salt, aromatic series iodonium salt, a metallocene compound, etc. [0049] Desirable photoinitiators are 2, 4, 6-trimethyl benzoyl diphenyl phosphine oxide, and a benzophenone. A thing well-known also as a thermal polymerization initiator is used, benzoyl peroxide, diisopropyl peroxy carbonate, lauroyl peroxide, tert-butyl peroxide (2-ethylhexanoate), azobisisobutyronitril, etc. are mentioned, and they are benzoyl peroxide and tert-butyl peroxide (2-ethylhexanoate) preferably.

[0050] When using a diisocyanate compound and a JIISO thiocyanate compound with the structural unit of a general formula (A2) and/or (B-2), and the poly thiol and a polyol compound as a constituent, Lewis bases, such as dibutyltin dilaurate, metallic compounds like aluminum TORIISO propoxide, tertiary amine, and the 3rd class phosphine, can be used as a catalyst of an urethane(thio)-ized reaction.

[0051] These initiators may use photo-curing and heat curing together the using two or more sorts together, and making it complete hardening whether you are Sumiya purpose, the rate of light and/or a thermal polymerization initiator -- a monomer or a constituent -- receiving -- 0.01 - 1 weight section extent -- it is 0.02 to 0.5 weight preferably. If there is too much blending ratio of coal of an initiator, the internal homogeneity of hardening resin is not only inferior, but a hue will get worse. When there is too little blending ratio of coal, it becomes impossible moreover, to fully stiffen a monomer or a constituent.

[0052] Moreover, in this invention, a hardening accelerator, a photosensitizer, an antioxidant, an ultraviolet ray absorbent, a coloring agent, a bulking agent, etc. can also be added and hardened if needed to the constituent before hardening. A well-known photopolymerization initiator and/or a well-known thermal polymerization initiator, and after a photosensitizer and a hardening accelerator are added further if needed, a monomer or a monomer constituent can close a light emitting diode component, and can obtain this invention light emitting diode.

[0053] If the approach of the closure is shown, as shown, for example in Fig. 1, this invention light emitting diode 1 can trickle a monomer or a monomer constituent, and can be made hemispherical so that a light-emitting part 4 may be laid underground on the substrate 3 of the light emitting diode component 2, and this invention light emitting diode 1 as shows this to drawing 3 as transparence resin 5 by carrying out polymerization hardening can be obtained. Moreover, as shown in Fig. 2, it can fix so that the light-emitting part 4 of the light emitting diode component 2 may be located in the center section in the mold cavity 7 for the size enlargement of the transparent metal mold 6, and the light emitting diode closed also by pouring in a monomer or a monomer constituent and carrying out polymerization hardening can be obtained.

[0054] As for hardening by the polymerization, it is desirable that a monomer and a

constituent are liquefied at a room temperature and the temperature of 80 degrees C or less in consideration of workability. If the mold in which the closure point had desired curvature is used although there is especially no limit about the configuration of a mold when using a die, a component can be cast as a lens with the closure. In case photo-curing is performed, ultraviolet, visible, and the activity energy line of an infrared region are used according to the property wavelength of a monomer and a constituent, a photopolymerization initiator, or a sensitizer, and are performed. In case heat curing is performed, it hardens at the temperature of the field doubled with the property of a monomer and a constituent, and a thermal polymerization initiator and a curing agent. In order to make it complete hardening whether you are Sumiya, these photo-curing and heat curing may be used together.

[0055] Although especially the light source or the heat source of an optical exposure at the time of performing light and/or heat curing are not limited, in performing photo-curing, when performing heat curing according to the property wavelength of a monomer or a photopolymerization initiator, according to the property of a monomer or a thermal polymerization initiator, it is chosen suitably. Although parallel light and the scattered light are irradiated using the ultraviolet-rays light sources, such as a high pressure mercury vapor lamp, a metal halide lamp, and a short arc lamp, and hardening is generally made when performing photo-curing, use of visible [, such as laser,] and the source of infrared light is also possible at concomitant use of a photosensitizer. The resin seals LED and LD obtained by this invention may process annealing by hardening afterbaking etc. in order to reduce the stress distortion inside resin, and an optical strain. Moreover, it is also possible to perform surface treatment, such as alternative ion and low-molecular diffusion, in a rebound ace court, an acid-resisting coat, dyeing, or the lens section.

[0056]

[Example] The following examples are for explaining this invention more concretely. In addition, the section in an example shows the weight section. Moreover, many properties of a hardened material given in an example were measured by the following examining method.

(1) Appearance : it is based on viewing.

(2) Refractive index N_d : Abbe refractometer (product made from ATAGO)

(3) Total luminous flux : 20mA constant current was impressed to LED, and the total luminous flux (unit: lm= lumen) emitted from an LED lamp was measured using the integrating sphere.

In addition, an LED chip given in an example is a periodic table. The thing of the double hetero structure which consists of Ga, aluminum, and As which are an III-V group was used. A refractive index is 3.52 and is red light emitting diode whose luminescent color is 650nm.

[0057] [Example 1] Churning mixing of the 2, 4, and 6-trimethyl benzoyl diphenyl phosphine oxide 0.1 section was carried out as a photopolymerization initiator at homogeneity, and it poured into the casting mold shown at drawing 2 at the p-screw (beta-methacryloiloxy-ethyl thio) xylylene 100 section. From the casting draw spike section, the LED chip with a terminal was fixed so that the light-

emitting part of each LED chip might be located in a constituent center section. In the distance of 40cm, the metal halide of output 80 W/cm which exists up and down performed UV irradiation in this whole mold for 3 minutes, and it was stiffened. The resin seal LED lamp which unmolds, cuts off one side of a terminal and is shown in drawing 3 was obtained. The total luminous flux of the obtained lamp was 0.20lm. On the other hand, it poured in the mold of optical polish glass using the silicon plate with a thickness of 2mm as a spacer, and it hardened like the above, the constituent was unmolded, and the test piece for refractometry was produced. The refractive index of the obtained hardened material was 1.60.

[0058] [Example 2] Instead of the p-screw (beta-methacryloiloxy-ethyl thio) xylylene 100 section, the 4 and 4'-screw (2-methacryloiloxy-ethyl thio) diphenylsulfone 100 section was used, and the LED lamp and the test piece for refractometry were obtained like the example 1. The total luminous flux of the obtained lamp was 0.25lm(s), and the refractive index of the obtained hardened material was 1.65.

[0059] [Example of a comparison] Instead of the p-screw (beta-methacryloiloxy-ethyl thio) xylylene 100 section, the tetraethylene glycol dimethacrylate 100 section was used and the LED lamp and the test piece for refractometry were obtained like the example 1. The total luminous flux of the obtained lamp was 0.95lm(s), and the refractive index of the obtained hardened material was 1.48.

Drawing 5 takes and plots the total luminous flux to which it is made an axis of abscissa from the refractive index of closure resin, and it makes outgoing radiation of examples 1 and 2 and the example of a comparison to an axis of ordinate from an LED lamp. By forming closure resin into a high refractive index shows that-izing of the LED lamp can be carried out [high brightness].

[Translation done.]

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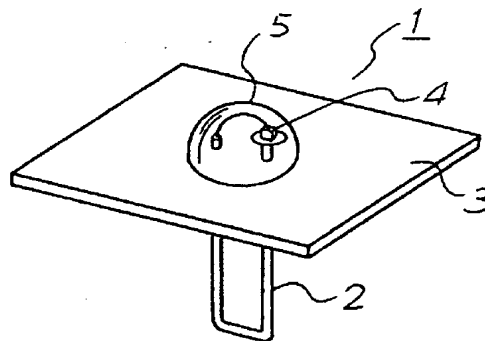
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(54) 【発明の名称】 樹脂封止高輝度発光ダイオード及びその製造方法

(57) 【要約】

【課題】 耐熱性で光輝度の発光ダイオードを得る。

【解決手段】 特定の構造単位の重合体からなる屈折率が1.55以上の透明樹脂によって発光部が封止された発光ダイオード。

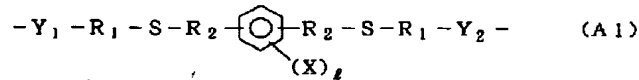


【特許請求の範囲】

【請求項1】 下記一般式（A1）および一般式（B1）より選ばれる少なくとも1種の構造単位の重合体か

らなる屈折率が1.55以上の透明樹脂によって少なくとも発光部が封止された発光ダイオード。

【化1】



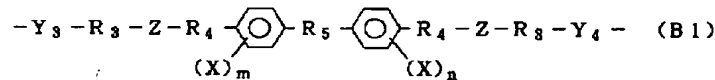
【式中 X：フッ素を除くハロゲン原子

1：0または1～4の整数

Y₁、Y₂：結合基で同じでも異なってもよい。

R₁、R₂：0または炭素数1～10のOまたはSを含んでもよいアルキレン基、アラルキレン基。】

【化2】



【式中 X：フッ素を除くハロゲン原子

m、n：0または1～4の整数

Z：OまたはS

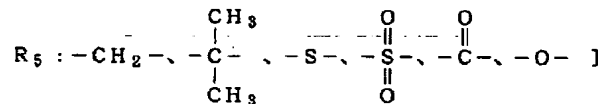
Y₃、Y₄：結合基で同じでも異なってもよい。

R₃：炭素数1～10のOまたはSを含んでもよい

アルキレン基、アラルキレン基

R₄：0または炭素数1～10のOまたはSを含んでもよいアルキレン基、アラルキレン基。

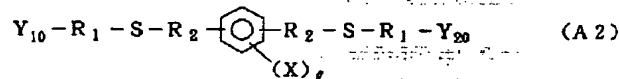
【化3】



【請求項2】 下記一般式（A2）および一般式（B2）より選ばれる少なくとも1種のモノマーに発光ダイオードの少なくとも発光部が浸漬した状態で光エネルギー線を照射して重合硬化せしめることにより、屈折率が

1.55以上の透明樹脂で少なくとも発光部を封止することを特徴とする発光ダイオードの製造方法。

【化4】



【式中 X：フッ素を除くハロゲン原子

1：0または1～4の整数

Y₁₀、Y₂₀：官能基で同じでも異なってもよい。

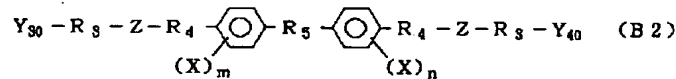
R₁、R₂：0または炭素数1～10のOまたはSを

含んでもよいアルキ

レン基、アラル

キレン基。】

【化5】



【式中 X：フッ素を除くハロゲン原子

m、n：0または1～4の整数

Z：OまたはS

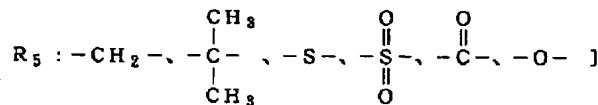
Y₃₀、Y₄₀：官能基で同じでも異なってもよい。

R₃：炭素数1～10のOまたはSを含んでもよい

アルキレン基、アラルキレン基

R₄：0または炭素数1～10のOまたはSを含んでもよいアルキレン基、アラルキレン基。

【化6】



【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は広告、照明、液晶パネル、あるいは光通信、光回路に使用されるLED、LD（レーザーダイオード）等の発光ダイオードに関するものである。特定の樹脂で発光ダイオードの半導体チップを封止することにより、高輝度であり、耐熱、耐湿、耐久性に優れるこれら素子を提供する。

【0002】

【従来の技術】 従来よりLED、LD等の発光ダイオードを樹脂により封止する提案が数多くなされている。その目的は大別して2つ挙げられる。1つは樹脂封止によ

リチップの外環境からの要因による劣化を阻止するためである。LED、LDチップは、発光時の発熱の影響もあって、廻りのガス、水分等の雰囲気により、表面が酸化劣化、反応劣化、付着劣化したり、断線を引き起こしたりするケースが多々ある。これらを樹脂封止により防止するものである。

【0003】他の目的は光取り出し効率を上げ、高輝度化を達成するためである。すなわち屈折率が2～6の発光ダイオード半導体チップと、屈折率が1.0の空気層との界面において光反射が行なわれ、チップからの放光が効率よく取り出せないという現象を緩和することである。この問題を解決するには、屈折率がチップと空気の間の中値を有する透明材質によりチップを封止することが必要である。透明材質としてはガラスまたは樹脂が挙げられるが、生産性を考慮し樹脂封止が一般的であり、特にエポキシ系熱硬化性樹脂による封止が多く提案されている。

【0004】しかしながらGaAs系材料に代表されるような周期律表のIII-V族よりなる半導体をはじめ工業的に使用される多くのLED、LDチップの屈折率は3～5付近であり、これらチップと空気層との界面反射を低減するのに最適な樹脂の屈折率は1.6～2.0とかなりの高屈折率樹脂を要求される。既存の封止樹脂は屈折率が1.4～1.5程度であり、十分な界面反射の低減、すなわち光取り出しが行なわれていなかった。なお本発明に記載の屈折率はNaのD線(589nm)を用いて25℃で測定した場合の値である。

【0005】

【発明が解決しようとする課題】本発明は高輝度で、耐熱性、耐湿性、耐久性に優れる樹脂封止発光ダイオードを生産性良く提供することを目的としたものである。発光ダイオードの輝度を高めるためには、発光した光を効率よく前面に取出すことが必要である。この点を更に詳細に述べれば、樹脂の屈折率と光取出効率は次のような関係にある。

【0006】すなわち、光取り出し効率は、LED、LDの材料である半導体の屈折率 n_0 と、封止樹脂の屈折率 n_1 、および外部環境すなわち通常は空気の屈折率 n_2 からそれぞれの界面における光の反射率を計算することにより求めることができ、それぞれの界面における反射率の総和が小さいほど光取り出し効率が高くなる。樹脂封止しない場合、この反射率 R_0 は近似的に次式

(1)で与えられる。

【0007】

【数1】

$$R_0 = \left(\frac{n_0 - n_2}{n_0 + n_2} \right)^2 \quad (1)$$

【0008】樹脂封止した場合の全反射率 R_1 は、チップー樹脂界面と樹脂ー外界界面の反射率の和であるから近似的に次式(2)で与えられる。

【0009】

【数2】

$$R_1 = \left(\frac{n_0 - n_1}{n_0 + n_1} \right)^2 + \left(\frac{n_1 - n_2}{n_1 + n_2} \right)^2 \quad (2)$$

【0010】ここでLED、LDチップの屈折率 n_0 として、周期律表のIII-V族よりなるGaAs系を例にとると、

$n_0 = 3.66$

また素子の外部環境は通常空気であるので、

$n_2 = 1.00$

とすると、樹脂封止しない場合の反射 R_0 は、(1)式より

$R_0 = 0.33$

となる。すなわち有効に取り出される光は、LED、LDチップの発光量の6.7%にすぎない。

【0011】一方高屈折率樹脂で封止した場合には、例えば n_1 が1.70の時を例にとると

$R_1 = 0.23$ ($n_0 = 3.66$, $n_1 = 1.70$, $n_2 = 1.00$)

となり、発光量の77%が取り出される。ちなみに反射率 R_1 が最小となるのは、(2)式より

【0012】

【数3】

【0013】の時である。すなわち上記の例($n_0 = 3.66$, $n_2 = 1.00$)の場合、 $n_1 = 1.91$ の時反射率は最小となり

$R_1 = 0.20$ 、

チップの発光量の80%が系外に取り出される。従って、高屈折率の半導体ダイオードを使用するときは、高屈折率の樹脂が必要となる。

【0014】また屈折率の異なる2つの樹脂を用いて、2段階でLED、LDチップを封止する際にも高屈折率とすることが有効である。すなわち直接チップに接する封止樹脂として高屈折率樹脂を用い、その上をおおう2段階目の封止樹脂として低屈折率のものを用いると、全反射率を更に低減できる。例えば1段階目に屈折率 $n_1 = 1.70$ の高屈折率樹脂を、2段階目に屈折率 $n_1' = 1.40$ の低屈折率樹脂を用いて封止した場合全反射率 R_2 は、前述のGaAs系を例にとると

【0015】

【数4】

$$R_2 = \left(\frac{n_0 - n_1}{n_0 + n_1} \right)^2 + \left(\frac{n_1 - n_1'}{n_1 + n_1'} \right)^2 + \left(\frac{n_1' - n_2}{n_1' + n_2} \right)^2 = 0.17$$

$$(n_0 = 3.66, n_1 = 1.70, n_1' = 1.40, n_2 = 1.00)$$

【0016】となり、光取り出し効率は83%となる。
 このように2段階以上で樹脂封止するに際しても、LED、LDチップに直接接する1段階目の樹脂は高屈折率であることが好ましい。以上LED、LDチップの光取り出し効率を界面反射率から推算してきたが、封止樹脂の高屈折率化は、チップー樹脂界面における全反射の角度すなわち臨界角を大きくして光取り出し効率の向上にも寄与する。図4に示すように、チップ面Dにおける全反射の臨界角 θ （垂直に対する角度）は、半導体層Aの屈折率 n_0 と、封止樹脂の屈折率 n_1 により、次式（4）に従って与えられる。

【0017】

【数5】

$$\theta = \sin^{-1} \left(\frac{n_1}{n_0} \right) \quad (4)$$

【0018】すなわち封止樹脂の屈折率が大きくなり n_1 が半導体層Aの屈折率 n_0 に近づくほど、臨界角 θ は大きくなり樹脂層Cへ出射する範囲は広がる。臨界角 θ は、例えば半導体チップとしてGaAs系（ $n_0 = 3.66$ ）を用いた場合、屈折率1.40の樹脂で封止した時は式（4）に従って、

$$\theta = 22.5^\circ$$

屈折率1.70の樹脂で封止した時は

$$\theta = 27.7^\circ$$

となる。この角度よりチップ面上の出射面積Sを次式（5）に従って求めることができる

【0019】

$$【数6】 S = \pi d \tan^2 \theta$$

【0020】ここでdは半導体層Aの厚みである。前述の屈折率1.40の樹脂で封止した場合の出射面積 S_1 、屈折率1.70の樹脂で封止した場合の出射面積 S_2 はそれぞれ

$$S_1 = 0.171 \pi d$$

$$S_2 = 0.275 \pi d$$

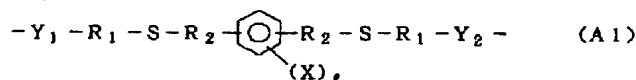
となり、樹脂の高屈折率化により出射面積が1.6倍程度広がることわかる。すなわち半導体チップのPN接合面から出射した光を効率良く取り出すことができる。

【0021】

【課題を解決するための手段】本発明者らは、上記課題を解決するために鋭意検討を行った結果、高屈折の特定の透明樹脂により発光ダイオードを封止することにより、光取り出し効率が向上し高輝度のLED、LD素子等の発光ダイオードが生産性よく得られることを見出した。また分子内に2個以上の重合性官能基を有する多官能光および／または熱硬化性樹脂を用いることにより、耐熱性、耐湿性、耐久性に優れる素子を製造することができる。本発明は下記一般式（A1）および一般式（B1）より選ばれる少なくとも一種以上の構造単位のある重合体からなる屈折率1.55以上の透明樹脂によって少なくとも発光部が封止された発光ダイオードにある。

【0022】

【化7】

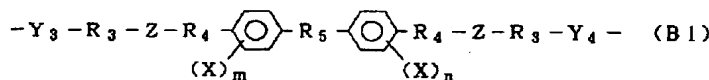


【0023】【式中 X：フッ素を除くハロゲン原子
 1：0または1～4の整数
 Y₁、Y₂：結合基で同じでも異なってもよい。
 R₁、R₂：0または炭素数1～10のOまたはSを含

んでもよいアルキレン基、アラルキレン基。】

【0024】

【化8】

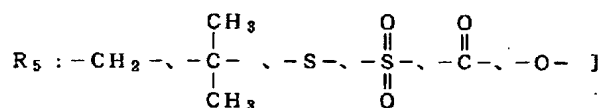


【0025】【式中 X：フッ素を除くハロゲン原子
 m、n：0または1～4の整数
 Z：OまたはS
 Y₃、Y₄：結合基で同じでも異なってもよい。
 R₃：炭素数1～10のOまたはSを含んでもよい

アルキレン基、アラルキレン基
 R₄：0または炭素数1～10のOまたはSを含んでもよいアルキレン基、アラルキレン基。

【0026】

【化9】



【0027】一般に樹脂の高屈折率化を達成するには、分子骨格や分子鎖に、①芳香環、②イオウ原子、③フッ素を除くハロゲン原子を導入すると効果的である。本発明者らは上記式(A1)、(B1)で式される構造単位を有する樹脂が高屈折率となることに注目し、これらの構造単位の両末端部に光および/または熱重合する官能基をそれぞれの末端に1個以上結合させることにより本発明に有効なモノマー(A2)、(B2)として使用で

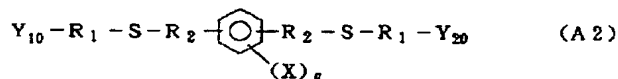
きることを確認した。

【0028】

【発明の実施の形態】本発明の封止樹脂として使用可能な屈折率1.55以上の透明樹脂は、下記一般式(A2)および一般式(B2)の透明性液体モノマーを、光および/または熱硬化させることにより得られる。

【0029】

【化10】

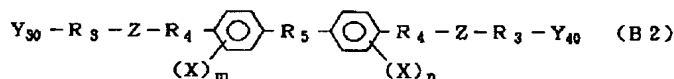


【0030】【式中 X: フッ素を除くハロゲン原子
1: 0または1~4の整数
Y₁₀、Y₂₀: 官能基で同じでも異なってもよい。
R₁、R₂: 0または炭素数1~10のOまたはSを含

んでいてもよいアルキレン基、アラルキレン基。】

【0031】

【化11】



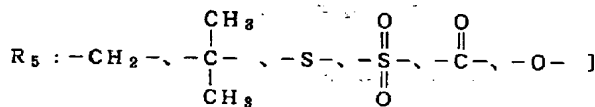
【0032】【式中 X: フッ素を除くハロゲン原子
m、n: 0または1~4の整数
Z: OまたはS
Y₃₀、Y₄₀: 官能基で同じでも異なってもよい。
R₃: 炭素数1~10のOまたはSを含んでいてもよい

アルキレン基、アラルキレン基

R₄: 0または炭素数1~10のOまたはSを含んでいてもよいアルキレン基、アラルキレン基。

【0033】

【化12】

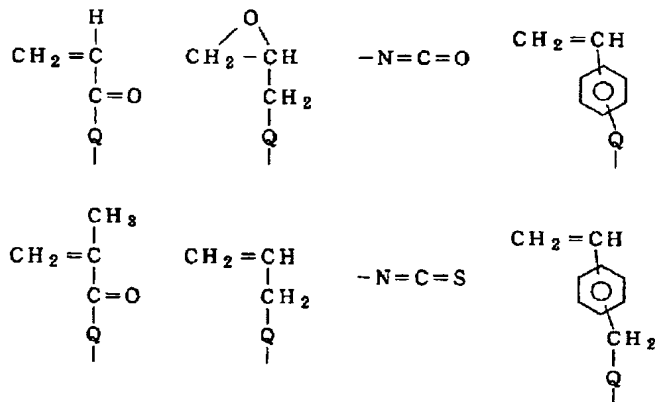


【0034】重合性官能基Y₁₀、Y₂₀、Y₃₀、Y₄₀としては、次式で示されるような(メタ)アクリロイル基、グリシジル基、アリール基、イソシアネート基、イソチオシアネート基、ビニルフェニル基、ビニルベンジル基等が挙げられる。これらのモノマーは分子内に2個以上

の重合性官能基を有する多官能性モノマーであり、その重合体は光硬化性樹脂あるいは熱硬化性樹脂として耐熱性、耐湿性に優れるものである。

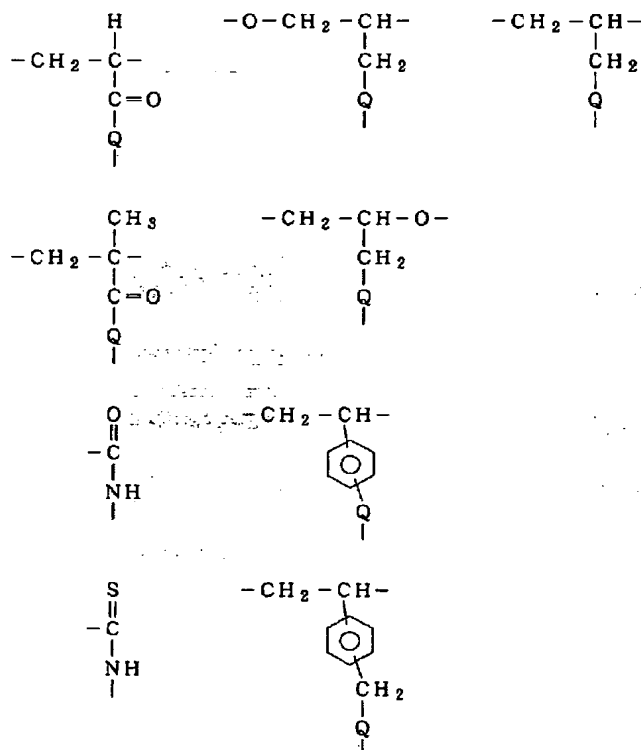
【0035】

【化13】



QはS又はO
 【0036】 従って、結合基Y₁、Y₂、Y₃、Y₄は、次の構造となる。

【0037】
 【化14】



QはS又はO

一般式(A2)の構造単位を有するモノマーとしては、例えば、p-ビス(β-(メタ)アクリロイルオキシエチルチオ)キシリレン、m-ビス(β-(メタ)アクリロイルオキシエチルチオ)キシリレン、p-ビス(β-(メタ)アクリロイルオキシエチルチオエチルチオ)キシリレン、m-ビス(β-(メタ)アクリロイルオキシエチルチオエチルチオ)キシリレン、p-ビス(β-(メタ)アクリロイルオキシエチルチオエチルチオ)キシリレン、p-ビス(β-(メタ)アクリロイルオキシエチルチオエチルチオ)キシリレン

キシリレン、m-ビス(β-(メタ)アクリロイルオキシエチルチオ)キシリレン、α, α'-ビス(β-(メタ)アクリロイルオキシエチルチオ)-2, 3, 5, 6-テトラクロロ-p-キシリレン、α, α'-ビス(β-(メタ)アクリロイルオキシエチルチオ)-2, 3, 5, 6-テトラクロロ-m-キシリレン、α, α'-ビス(β-(メタ)アクリロイルオキシエチルチオ)-2, 3, 5, 6-テトラクロロ-p-キシリレン

[illegible]

【0041】4, 4'-ビス(2-グリシジルオキシエチルチオ)ジフェニルスルホン、4, 4'-ビス(2-グリシジルオキシエチルオキシ)ジフェニルスルホン、2, 2-ビス[4-(β-グリシジルオキシエチルチオ)フェニル]プロパン、2, 2-ビス[4-(β-グ

[0045] 4, 4'-ビス〔2-(4-ビニルフェニルオキシ)エチルチオ〕ジフェニルスルホン、4, 4'-ビス〔2-(4-ビニルフェニルオキシ)エチルオキシ〕ジフェニルスルホン、2, 2-ビス〔4-{2-(4-ビニルフェニルオキシ)エチルチオ}フェニル〕プロパン、2, 2-ビス〔4-{2-(4-ビニルフェニルオキシ)エチルオキシ}フェニル〕プロパン、4, 4'-ビス〔2-(4-ビニルフェニルチオ)エチルチオ〕ジフェニルスルホン、4, 4'-ビス〔2-(4-ビニルフェニルチオ)エチルオキシ〕ジフェニルスルホン、2, 2-ビス〔4-{2-(4-ビニルフェニルチオ)エチルチオ}フェニル〕プロパン、2, 2-ビス〔4-{2-(4-ビニルフェニルチオ)エチルオキシ}フェニル〕プロパン、4, 4'-ビス〔2-(4-ビニルベンジルオキシ)エチルチオ〕ジフェニルスルホン、4, 4'-ビス〔2-(4-ビニルベンジルオキシ)エチルオキシ〕ジフェニルスルホン、2, 2-ビス〔4-{2-(4-ビニルベンジルオキシ)エチルチ

オ] フェニル] プロパン、2, 2-ビス {4- [2- (4-ビニルベンジルオキシ) エチルオキシ] フェニル] プロパン、4, 4'-ビス [2- (4-ビニルベンジルチオ) エチルチオ] ジフェニルスルホン、4, 4'-ビス [2- (4-ビニルベンジルチオ) エチルオキシ] ジフェニルスルホン、2, 2-ビス {4- [2- (4-ビニルベンジルチオ) エチルチオ] フェニル] プロパン、2, 2-ビス {4- [2- (4-ビニルベンジルチオ) エチルオキシ] フェニル] プロパン} のようなスチレン系化合物が挙げられる。

【0046】これらの中で好ましいのはジ (メタ) アクリレート化合物であり、特に好ましいのはp-ビス (β-メタクリロイルオキシエチルチオ) キシリレン、p-ビス (β-メタクリロイルチオエチルチオノキシリレン、4, 4'-ビス (2-メタクリロイルオキシエチルチオ) ジフェニルスルホン、4, 4'-ビス (2-メタクリロイルチオエチルチオ) ジフェニルスルホン、およびこれらのモノマーと共重合可能なモノマーとの組成物である。

【0047】一般式 (A2) および/または一般式 (B2) の構造単位を有するモノマーと共重合可能なモノマーとしては、例えば、メチル (メタ) アクリレート、フェニル (メタ) アクリレート、2-ヒドロキシエチル (メタ) アクリレート、メタクリロイルオキシメチルテトラシクロデカン、メタクリロイルオキシメチルテトラシクロデセン、エチレングリコールジ (メタ) アクリレート、1, 6-ヘキサジオールジ (メタ) アクリレート、2, 2'-ビス {4- (β-メタアクリロイルオキシエトキシ) シクロヘキシル} プロパン、1, 4-ビス (メタアクリロイルオキシメチル) シクロヘキサジ、トリメチロールプロパントリ (メタ) アクリレート、スチレン、クロルスチレン、α-メチルスチレン、ジビニルベンゼンのようなアクリレート化合物やスチレン系化合物、ペンタエリスリトールテトラキス (β-チオプロピオネート)、ペンタエリスリトールテトラキス (β-チオグリコレート)、トリメチロールプロパントリス (β-チオプロピオネート)、トリメチロールプロパントリス (β-チオグリコレート)、ジエチレングリコールビス (β-チオプロピオネート)、ジエチレングリコールビス (β-チオグリコレート)、トリエチレングリコールビス (β-チオプロピオネート)、トリエチレングリコールビス (β-チオグリコレート)、ジペンタエリスリトールヘキサキス (β-チオプロピオネート)、ジペンタエリスリトールヘキサキス (β-チオグリコレート)、トリス [2- (β-チオプロピオニルオキシ) エチル] トリイソシアヌレート、トリス [2- (β-チオプロピオニルオキシエトキシ) エチル] トリイソシアヌレート、トリス [3- (β-チオプロピオニルオキシ) プロピル] トリイソシアヌレート、トリス (2-チオグリコニルオキシエチル) トリイソシアヌレート、トリス (2-チオグリコニルオキシエチル) トリイソシアヌレート、トリイソシアヌレート、トリス (3-チオグリコニルオキシエチル) トリイソシアヌレート、ベンゼンジメルカプタン、キシリレンジメルカプタン、4, 4'-ジメルカプトジフェニルスルフィドのポリチオール、および公知のポリオール等が挙げられる。一般式 (A2) および/または (B2) の構造単位を有するモノマーとしてジイソシアネート化合物やジイソチオシアネート化合物を用いた場合には、これらの化合物と付加重合するポリチオールもしくはポリオール化合物が好ましい。使用するポリチオールもしくはポリオールの量は、その全官能基数がイソシアネートもしくはイソチオシアネートの全官能基数とほぼ同じになるよう設定する。

【0048】これら一般式 (A2) および/または一般式 (B2) の構造単位を有するモノマーと共重合可能なモノマーの使用量は、重量比率が全組成の80%以下で、組成物を硬化した樹脂の屈折率が1.55以上になるよう設定される。これらの組成物を光および/または熱硬化させる際使用される開始剤としては、例えば光重合剤として公知のラジカル重合開始剤、カチオン重合開始剤が使用されるが、2, 6-ジメチルベンゾイルジフェニルホスフィンオキシド、2, 4, 6-トリメチルベンゾイルジフェニルホスフィンオキシド、2, 4, 6-トリメチルベンゾイルフェニルホスフィン酸メチルエステル、2, 6-ジクロロベンゾイルフェニルホスフィンオキシド、2, 6-ジメチルトキシベンゾイルジフェニルホスフィンオキシド等のアシルホスフィンオキシドおよびアシルホスフィン酸エステル類、1-フェニル-2-ヒドロキシ-2-メチルプロパン-1-オン、1-ヒドロキシシクロヘキシルフェニルケトン、4-ジフェノキシシクロアセトフェノン、ジエトキシアセトフェノン、1- (4-イソプロピルフェニル) -2-ヒドロキシ-2-メチルプロパン-1-オン等のアセトフェノン系化合物、およびベンゾフェノン、4-フェニルベンゾフェノン、ベンゾイル安息香酸メチルチ、4-フェニルベンゾフェノン、ヒドロキシベンゾフェノン、3, 3'-ジメチル-4-メトキシベンゾフェノン、ジフェノキシベンゾフェノン等のベンゾフェノン系化合物、芳香族ジアゾニウム塩、芳香族スルホニウム塩、芳香族ヨードニウム塩、メタロセン化合物等がある。

【0049】好ましい光開始剤は、2, 4, 6-トリメチルベンゾイルジフェニルホスフィンオキシド、ベンゾフェノンである。熱重合開始剤としても公知のものが使用され、ベンゾイルパーオキシド、ジイソプロピルパーオキシカーボネート、ラウロイルパーオキシド、t-ブチルパーオキシ (2-エチルヘキサノエート)、アゾビスイソプロチロニトリル等が挙げられ、好ましくはベンゾイルパーオキシド、t-ブチルパーオキシ (2-エチルヘキサノエート) である。

【0050】組成物として、一般式 (A2) および/ま

たは(B2)の構造単位を持つジイソシアネート化合物やジイソチオシアネート化合物と、ポリチオール、ポリオール化合物を用いる場合は、ジブチルチンジラウレート、アルミニウムトリイソプロポキシドのような金属化合物、3級アミンや3級ホスフィン等のルイス塩基を(チオ)ウレタン化反応の触媒として用いることができる。

【0051】これら開始剤は2種以上を併用してもよく、また硬化をすみやかに完結させる目的で光硬化と熱硬化を併用してもよい。光および/または熱重合開始剤の割合はモノマーまたは組成物に対して、0.01~1重量部程度、好ましくは、0.02~0.5重量部である。開始剤の配合割合が多すぎると、硬化樹脂の内部均質性が劣るだけでなく、色相も悪化する。また配合割合が少なすぎると、モノマーまたは組成物を十分に硬化させることができなくなる。

【0052】また本発明においては、硬化前の組成物に必要に応じ、硬化促進剤、光増感剤、酸化防止剤、紫外線吸収剤、着色剤、充てん剤等を添加して硬化することもできる。モノマーもしくはモノマー組成物は公知の光重合開始剤および/または熱重合開始剤、更には必要に応じて光増感剤や硬化促進剤を添加された後、発光ダイオード素子を封止して本発明発光ダイオードを得ることができる。

【0053】封止の方法を示せば、例えば第1図に示すように本発明発光ダイオード1は、発光ダイオード素子2の基板3上に、発光部4が埋設されるようにモノマー又はモノマー組成物を滴下して半球状とし、これを重合硬化することによって透明樹脂5として図3に示すような本発明発光ダイオード1を得ることができる。また、第2図に示すように透明な金型6の賦形用キャビティ7内中央部に発光ダイオード素子2の発光部4が位置するように固定して、モノマー又はモノマー組成物を注入して重合硬化することによっても封止した発光ダイオードを得ることができる。

【0054】重合による硬化は、作業性を考慮し、モノマーおよび組成物は室温および80℃以下の温度で液状であることが好ましい。成形型を用いる場合、型の形状に関しては特に制限はないが、封止先端部が所望の曲率を持った型を用いると、封止とともに素子をレンズとして成型できる。光硬化を行う際には、紫外、可視、赤外線領域の活性エネルギー線を、モノマーおよび組成物と光重合開始剤や増感剤の特性波長に合わせて使用して行う。熱硬化を行う際には、モノマーおよび組成物と熱重合開始剤や硬化剤の特性に合わせた領域の温度にて硬化を行う。すみやかに硬化を完了させるために、これら光硬化と熱硬化を併用してもよい。

【0055】光および/または熱硬化を行う際の、光照射の光源や熱源は特に限定されないが、光硬化を行う場合には、モノマーや光重合開始剤の特性波長に応じて、

熱硬化を行う場合には、モノマーや熱重合開始剤の特性に応じて適宜選択される。一般的には、光硬化を行う場合には高圧水銀灯、メタルハライドランプ、ショートアークランプ等の紫外線光源を用いて平行光、散乱光を照射して硬化がなされるが、光増感剤の併用でレーザー等の可視、赤外光源の使用も可能である。本発明により得られた樹脂封止LED、LDは、樹脂内部の応力歪や光学歪を低減させるために、硬化後加熱によるアニール等の処理を行ってもよい。またハードコート、反射防止コート、染色あるいはレンズ部に選択的なイオン、低分子拡散等の表面処理を行うことも可能である。

【0056】

【実施例】以下の実施例は本発明をより具体的に説明するためのものである。なお例中の部は重量部を示す。また実施例に記載の硬化物の諸特性は下記の試験法により測定した。

(1) 外観：目視による。

(2) 屈折率Nd：アッペ屈折計（アタゴ社製）

(3) 全光束：LEDに20mAの定電流を印加して、積分球を用いて、LEDランプより発せられる全光束（単位：lm=ルーメン）を測定した。

なお実施例記載のLEDチップは、周期律表のIII-V族であるGa、Al、Asよりなるダブルヘテロ構造のものを用いた。屈折率は3.52であり、発光色が650nmの赤色発光ダイオードである。

【0057】〔実施例1〕p-ビス（β-メタクリロイルオキシエチルチオ）キシリレン100部に、光重合開始剤として2,4,6-トリメチルベンゾイルジフェニルホスフィンオキシド0.1部を均一に攪拌混合して、図2に示される注型型に注入した。注型型上部より端子付きLEDチップを、それぞれのLEDチップの発光部が組成物中央部に位置するように固定した。この型全体に、距離40cmで上下にある出力80W/cmのメタルハライドにより3分間紫外線照射を行い硬化させた。脱型して端子の一方を切り取り図3に示される樹脂封止LEDランプを得た。得られたランプの全光束は、0.20lmであった。一方組成物を、スぺーサーとして厚さ2mmのシリコン板を用いた光学研磨ガラスの型に注液し、上記と同様にして硬化を行い、脱型して屈折率測定用の試験片を作製した。得られた硬化物の屈折率は1.60であった。

【0058】〔実施例2〕p-ビス（β-メタクリロイルオキシエチルチオ）キシリレン100部の代わりに、4,4'-ビス（2-メタクリロイルオキシエチルチオ）ジフェニルスルホン100部を用いて実施例1と同様にしてLEDランプと屈折率測定用試験片を得た。得られたランプの全光束は0.25lmであり、得られた硬化物の屈折率は1.65であった。

【0059】〔比較例〕p-ビス（β-メタクリロイルオキシエチルチオ）キシリレン100部の代わりに、テ

トラエチレングリコールジメタクリレート100部を用いて実施例1と同様にして、LEDランプと屈折率測定用試験片を得た。得られたランプの全光束は0.95lmであり、得られた硬化物の屈折率は1.48であった。図5は実施例1、2、および比較例を、横軸に封止樹脂の屈折率、縦軸にLEDランプより出射する全光束をとってプロットしたものである。封止樹脂を高屈折率化することによりLEDランプを高輝度化できることがわかる。

【図面の簡単な説明】

【図1】本発明発光ダイオードを製造する方法を示す斜視図

【図2】他の製造法を示す斜視図

【図3】本発明発光ダイオードの例を示す斜視図

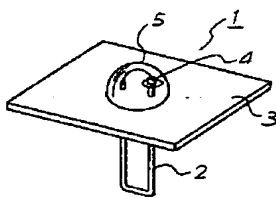
【図4】屈折率による光取出効率を示す説明図

【図5】透明樹脂の屈折率と取出光束の関係を示す図

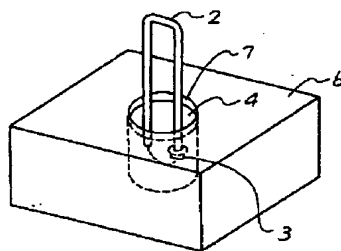
【符号の説明】

- 1 発光ダイオード
- 2 発光ダイオード素子
- 3 基板
- 4 発光部
- 5 透明樹脂
- 6 金型
- 7 金型キャビティー

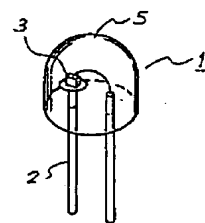
【図1】



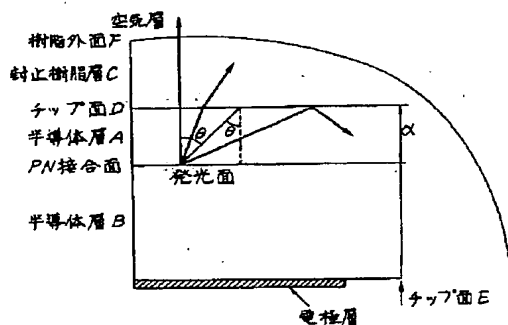
【図2】



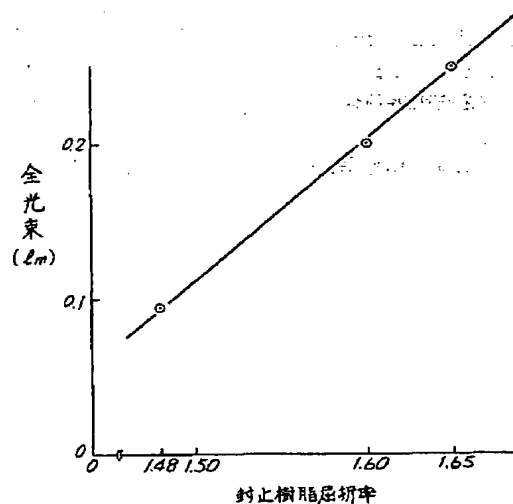
【図3】



【図4】



【図5】



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